



Infrared studies of CO oxidation by oxygen and by water over Pt/Al₂O₃ and Pd/Al₂O₃ catalysts

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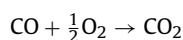
ABSTRACT

CO adsorption has been studied over Pd/Al₂O₃ and Pt/Al₂O₃ catalysts using IR spectroscopy in different conditions and after different pretreatments. The oxidation of CO by oxygen and water (water gas shift) has also been studied at 130–673 K. The spectra show that the most active species as oxidant for CO are dispersed Ptⁿ⁺ and Pdⁿ⁺ cations and PdO_x species mainly “decorating” the defects of alumina crystals where they modify completely the behaviour of surface OH's and Lewis acid sites. Some of these species oxidize CO to CO₂ already below ~200 K. These highly oxidized species escape detection by IR during reaction at 500–673 K, when only reduced sites are apparent due to their very strong interaction with CO. The data suggest that redox mechanisms could occur for both WGS and CO oxidation occurring on highly dispersed cationic species non detectable under reaction conditions.

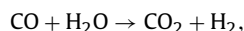
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1. Introduction

The low temperature CO oxidation reaction



and the low temperature water gas shift (LTWGS) reaction



represent relevant steps in some very important processes of both environmental and industrial interest such as to abate CO in the preparation of pure H₂ for hydrogenation reactions and fuel cell applications [1,2]. CO oxidation can also be used to purify waste gases.

The two reactions have some parallelism, being in both reactions CO oxidized to CO₂, either by oxygen or by water. This parallelism is somehow supported by the similarity of the catalysts which are active in the two reactions. Copper and noble metal catalysts are the main active components of catalysts for CO oxidation at low temperature (373–473 K) [3], as well as for LTWGS [4–6]. In the last case, noble metal based catalysts are needed when pyrophoricity

typical of Cu–ZnO–Al₂O₃ LTWGS catalysts has to be avoided, as in the case of small size fuel cell applications.

Pt/Al₂O₃ based catalysts are good catalysts for water gas shift reaction for fuel cell applications [4–8], although Pt catalysts based on reducible supports appear to be even more active. Pt/Al₂O₃ is also active for low temperature CO oxidation [9] and, usually promoted by iron, represents the main composition of commercial catalysts for preferential CO oxidation (PROX) [2,10], i.e. the oxidation of CO to CO₂ in the presence of hydrogen.

Pd/Al₂O₃ is even more active in low temperature CO oxidation than Pt/Al₂O₃ [11], but loses CO oxidation activity in the presence of hydrogen, thus being not applicable for the PROX reaction [12]. Pd/Al₂O₃ is reported to be an active catalyst too for the WGS reaction, although less than other supported noble metal catalysts [7]. However, activation energy for the WGS reaction is on supported Pd lower than on other supported noble metals. On the other hand, the catalytic activity of Pd/γ-Al₂O₃ is strongly enhanced by the co-presence of Zn for WGS [13].

Characterization of noble metal based WGS and CO oxidation catalysts is normally done in terms of metal dispersion and metal particle size. Such properties may be in fact measured by characterization techniques such as Transmission Electron Microscopy, X-Ray diffraction and adsorption of probe molecules. Several *operando* and *in situ* IR studies have been reported recently on both CO oxidation [9,14–17] and WGS [8,18–21] over noble metal catalysts. All these studies confirm the presence of metallic

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particles during the reactions. However, dispersed metal or cationic species may also be present on the catalyst surface, as observed, e.g. using IR spectroscopy of adsorbed CO [22], but these species escape characterization techniques such as TEM and XRD.

In the present paper we will discuss our *in situ* IR studies in connection with *operando* IR studies and surface science studies to have more information on the role of the metal species actually present at the catalyst surface and possibly active in the reactions. According to the literature, the activity of the supported noble metal catalysts may be strongly modified by the presence of base metals added as promoters [2] and even present on alumina at the impurity level. We used here virtually pure, commercial γ -alumina samples, as supports. To improve stability, needed for repeated shut-down/start up operation typical of fuel cell application, the support for WGS catalysts was previously calcined to obtain θ - Al_2O_3 with reduced surface area (near $100 \text{ m}^2/\text{g}$).

2. Experimental

Pt/ γ - Al_2O_3 catalyst (Pt: $\sim 1 \text{ wt}\%$) was obtained by impregnation of a commercial γ - Al_2O_3 carrier (Versal 250 from UOP, surface area of $200 \text{ m}^2/\text{g}$ and pore volume near $1 \text{ cm}^3/\text{g}$) with a solution of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ (Strem Chemicals, 5% Pt in ammonium hydroxide) with an appropriate concentration so as to yield 1 wt% Pt metal loading. After drying in air for 12 h at 80°C calcination at 500°C for 5 h was performed. Palladium supported on alumina catalyst (Pd: $\sim 2 \text{ wt}\%$) was prepared starting from a commercial alumina (Sasol Puradox SBA140) calcined at 1223 K for 10 h in air in order to stabilize structural and morphological properties. A θ - Al_2O_3 (with traces of α - Al_2O_3) phase was obtained with a specific surface area of $100 \text{ m}^2/\text{g}$ and a pore volume of $0.49 \text{ cm}^3/\text{g}$. Palladium was added by a dry impregnation technique, starting from an aqueous solution containing the $\text{Pd}(\text{NO}_3)_2$ precursor (Alfa Aesar) in appropriate amounts. The prepared catalyst was dried at 383 K for 2 h and treated at 873 K for 10 h in air before any testing.

For IR studies, pressed disks of the pure catalysts powders were activated “*in situ*” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. Pd-based catalyst was first submitted to a treatment in air for 30 min, followed by evacuation at 623 K or 773 K before the adsorption experiments. In order to obtain the reduced catalysts, after the mentioned evacuation, they were put in contact with a H_2 pressure $\sim 400 \text{ Torr}$ at 623 or 773 K , for 30 min, and successively outgassed at the same temperature, unless otherwise specified. Pt-based catalyst was outgassed

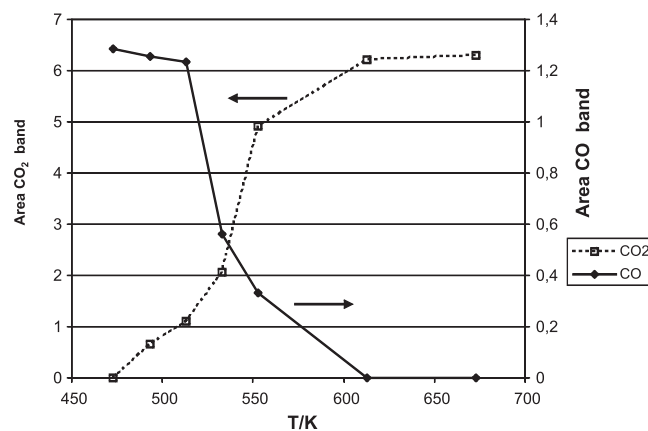


Fig. 1. Trends of the intensities of the gas phase CO band (2142 cm^{-1}) and CO_2 band (2349 cm^{-1}) upon CO oxidation experiment over 1% Pt/ γ - Al_2O_3 catalyst.

and reduced at 623 K or 773 K . Over both materials, CO adsorption was performed at 133 K by the introduction of a known dose of the gas (10 Torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected, evacuating at increasing temperatures between 133 K and 273 K . Spectra have been recorded in the temperature range 133 K /room temperature or even upon heating using a Nicolet Nexus FT instrument.

WGS as well as CO oxidation studies have been performed in the IR cell by admitting controlled low pressures of the reactants at room temperature (CO 8 Torr + H_2O vapour 11 Torr for WGS, CO 8 Torr + O_2 12 Torr for CO oxidation) then increasing temperature. Spectra of the gas and of the catalyst were taken alternatively upon increasing temperature.

3. Results

According to the literature, both Pt/ Al_2O_3 and Pd/ Al_2O_3 catalysts are active for CO oxidation at $\sim 450 \text{ K}$. We performed CO oxidation experiments in our IR cell. In Fig. 1 data are reported concerning CO oxidation on Pt/ Al_2O_3 . The curves relative to the integrated intensities of the CO rotovibrational band centred at 2142 cm^{-1} and of CO_2 rotovibrational band centred at 2349 cm^{-1} show the total conversion of CO into CO_2 in the range 473 – 573 K . During the reaction (Fig. 2), the spectra of the adsorbed species have also been recorded. They show a band centred at 2070 cm^{-1} , with a component at 2047 cm^{-1} more evident at lower temperatures,

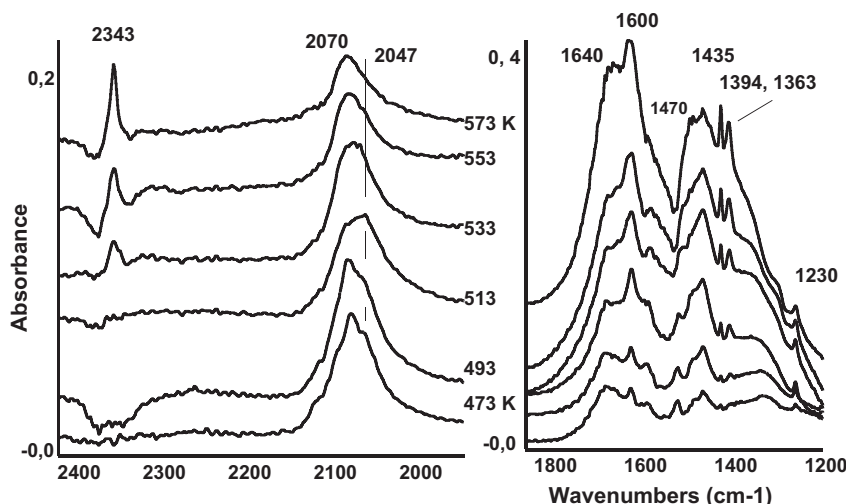


Fig. 2. FT-IR spectra of the adsorbed species upon CO oxidation experiment over 1% Pt/ γ - Al_2O_3 catalyst.

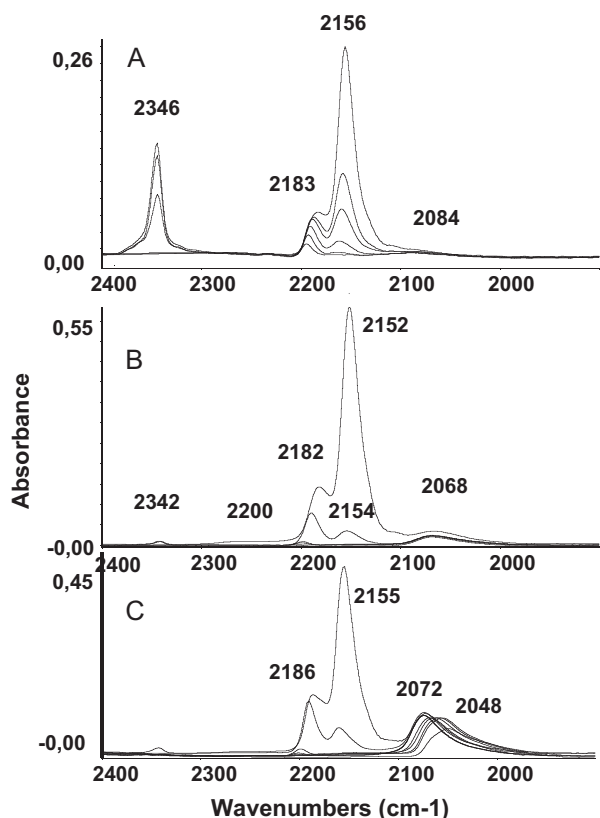


Fig. 3. FT IR spectra of CO adsorbed at 133 K on 1% Pt/ γ -Al₂O₃ catalyst: (A) after simple outgassing at 623 K; (B) after reduction in hydrogen at 623 K and (C) after reduction in hydrogen at 773 K.

certainly due to terminal Pt⁰ carbonyls. In the lower frequency region bands due to formate species (1600, 1394, 1363 cm⁻¹) and to two different bicarbonate species (1640, 1470, 1435, 1230 cm⁻¹) are also observed (Fig. 2, right). The results are quite similar to those observed upon *operando* studies by Daniel et al. [14,17]. Similar spectra with the detection only of terminal carbonyls on metallic Pt (2084–2053 cm⁻¹) have been reported in low temperature *in situ* adsorption and oxidation studies over Pt/Al₂O₃ catalysts [9,23]. This shows that our experimental conditions are actually not so different from those applied in these studies.

In Fig. 3 the spectra of CO adsorbed at low temperature over this catalyst after simple outgassing at 623 K, after reduction in hydrogen at 623 K and after reduction in hydrogen at 773 K are reported, together with their evolution upon warming. In Fig. 4 the spectra obtained after outgassing adsorbed CO at 133 K in the three conditions are compared. After the stronger reduction treatment a strong band associated with terminal carbonyls over reduced Pt centres is evident. This band shifts upon outgassing during warming from 2072 cm⁻¹ to 2048 cm⁻¹ (as usual due to the decrease of static and dynamic coupling effects) and is still present after outgassing at 473 K. This shows how resistant are carbonyls on Pt metal species. This band is much weaker after reduction at 623 K and almost absent after simple outgassing at 623 K. However, under these conditions CO is oxidized to CO₂, as evident from the appearance of a band at 2346 cm⁻¹ on top of Fig. 3, due to the OCO asymmetric stretching of non-rotating (thus adsorbed) carbon dioxide. This shows that, in these conditions, strongly oxidizing Ptⁿ⁺ centres are present, together with active oxide species.

The comparison of the spectra obtained after outgassing adsorbed CO at 133 K shows that the more reduced the sample is, the more intense is also the band at 2190–2185 cm⁻¹. This band is assigned predominantly to CO interacting with alumina's Lewis

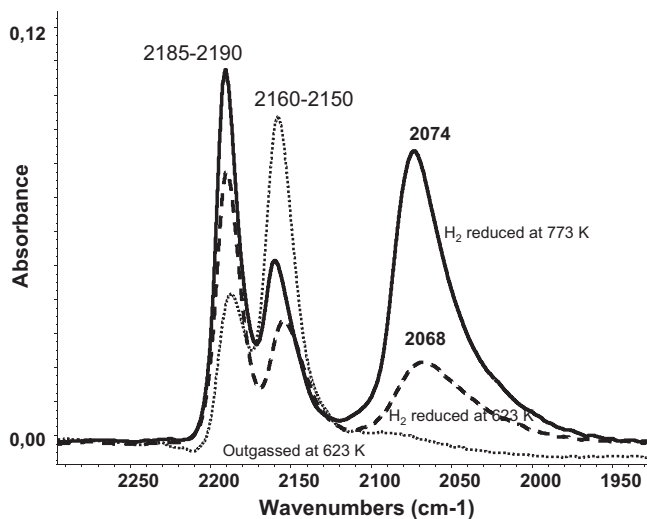


Fig. 4. FT IR spectra of CO adsorbed at 133 K upon outgassing after three different pretreatments on 1% Pt/ γ -Al₂O₃ catalyst: a comparison.

sites, Al³⁺ ions. According to previous studies, dispersed Pt oxide species interact with the more reactive sites of the support surface, where both Lewis sites and OH's are located. Reduction implies production of water (and his desorption) as well as diffusion of Pt to coalesce into metal particles. This makes free alumina's Lewis sites and surface OH's.

The behaviour of the band at 2160–2150 cm⁻¹ is more complex. It first decreases markedly, then increases shifting up a little bit. This can be interpreted as a result of superimposition of the band of H-bonded CO with another band, i.e. CO interacting with oxidized Pt ions. The latter, which is located at lower frequencies, decreases by reduction while the former increases due to the reappearance of surface OH's become free as the result of reduction.

In Fig. 5 the spectra of CO adsorbed on the Al₂O₃ support, on unreduced Pt/Al₂O₃ and on mildly reduced Pt/Al₂O₃ and their deconvolutions are reported. The deconvolution of the spectrum of CO adsorbed on alumina allows to only separate the component due to CO interacting with Al³⁺, found at 2183 cm⁻¹, from that due to CO H-bonded on OH's, found at 2152 cm⁻¹. In the case of the spectrum of CO adsorbed on unreduced Pt/Al₂O₃ the higher frequency band increases in intensity and shifts up to 2186 cm⁻¹, the most intense band shifts up a little bit to 2155 cm⁻¹ while a new absorption appears clearly centred at 2135 cm⁻¹. In the case of reduced Pt/Al₂O₃ the higher frequency band shifts back down to 2183 cm⁻¹ and decreases in intensity, the most intense band shifts shifts also back to 2153 cm⁻¹, while the new absorption increases in intensity and shifts up to 2139 cm⁻¹.

These data suggest that highly oxidized and oxidizing Pt ions contribute to the band at 2186 cm⁻¹, and are reduced in the reduced sample. We assign the band at 2186 cm⁻¹ to Ptⁿ⁺-CO (with $n=4$ or 2). The band at 2135–2139 cm⁻¹ should be assigned to another form of Ptⁿ⁺-CO, less oxidized and less oxidant, with $n=2$ or 1. The amount of the latter species should increase by reduction of the former one. These assignments are consistent with data arising from different authors (reviewed in Ref. [22]) as well as with previous studies from one of our laboratories [24–26].

The comparison of the spectra reported in Figs. 2–5 shows again that the weaker interactions, such as CO interaction with Al³⁺, Ptⁿ⁺ and with the hydroxyl groups, cannot be detected at room or higher temperatures, being very labile. This means that the equilibrium involved in these interactions, is displaced towards the gas phase CO at room or higher temperatures. However, this does not mean that the surface species involved in these interactions do not exist in

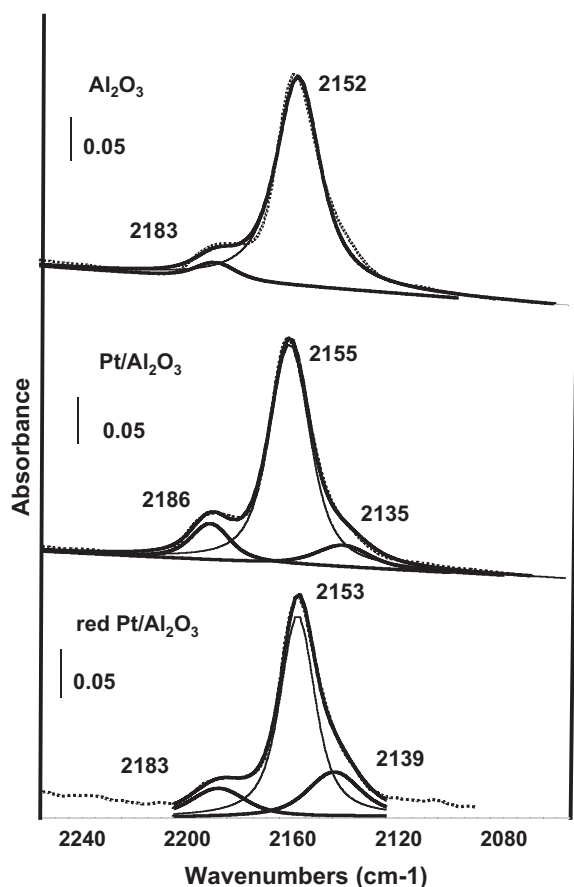


Fig. 5. FT-IR spectra of CO adsorbed on γ - Al_2O_3 support, on unreduced and pre-reduced 1% Pt/ γ - Al_2O_3 at -140°C at saturation, and deconvolution of the spectra.

these conditions. Additionally, a labile species, even if its concentration is very small, may be involved in the fast steps of the reaction. The spectra recorded at r.t. or higher temperatures, including upon CO oxidation reaction, only reveal the stronger interactions, i.e. CO bonded to Pt° . These species are detected but this does not mean that active interactions are revealed.

We investigated the WGS reaction the behaviour over Pd/ Al_2O_3 in our IR cell. Reaction started to be detectable at 630 K. In Fig. 6, insert, the difference spectrum of the gas phase is reported (spectrum recorded at 630 K – spectrum recorded at 573 K), where the consumption of gas phase CO and H_2O is evident (negative rovibrational bands are present in the subtraction spectrum at 2142 cm^{-1} and 1595 cm^{-1}) producing CO_2 (positive rovibrational band in the subtraction at 2349 cm^{-1}). The spectra of the catalyst at 573 K (i.e. when reaction is still not detected) and at 673 K (when reaction occurs) are reported in Fig. 6a and b. The spectrum recorded at 573 K shows a CO stretching band centred at 1875 cm^{-1} with a shoulder at 1868 cm^{-1} . When reaction goes, at 673 K, the spectrum is different with a main component, complex, in the region $1970\text{--}1940\text{ cm}^{-1}$ (main maximum at 1955 cm^{-1}) and a second pronounced component at 1912 cm^{-1} . In Fig. 6c the spectrum of Pd/ Al_2O_3 sample after reduction in hydrogen at 773 K, and contact with CO at room temperature, is reported. This is the typical spectrum of reduced Pd/ Al_2O_3 with the main band at 1986 cm^{-1} , due to bridging Pd carbonyls, the evident asymmetric peak at 2087 cm^{-1} , due to terminal Pd carbonyls and another broad component at 1935 cm^{-1} , due to either a second family of bridging carbonyls or to threefold bridging carbonyls [27].

The spectra observed upon WGS reaction are similar to those recorded at room temperature over the reduced surface, showing

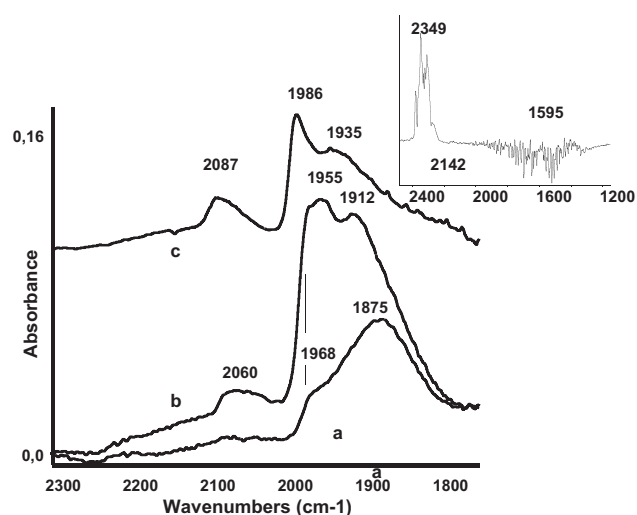


Fig. 6. FT-IR spectra (CO stretching region) of the 2% Pd/ θ - Al_2O_3 catalyst during WGS reaction experiment ($\text{CO} + \text{H}_2\text{O}$ vapour, 573 K (a) and 633 K (b)). In the insert: difference spectrum of the gas phase, 633–573 K. (c) CO adsorbed at r.t. over the catalyst after prolonged treatment in H_2 at 773 K.

bridging and threefold bridging Pd carbonyls together with few terminal carbonyls, although different populations or slightly different structures should exist, to justify different position and intensities of the carbonyl bands. This suggests that during the reaction the catalyst is indeed reduced, at least in part.

During this experiment, extremely weak absorption at 1594, 1392 and 1375 cm^{-1} , possibly due to formate species, can be seen but their maximum intensity ($\Delta\text{Absorbance} \sim 0.03$) is not far from noise and similar to those of other absorptions in the carbonate–bicarbonate region. In any case these species start to be detected at 473 K, have their maximum at 610 K and are fully disappeared at 673 K.

In Figs. 7–10 the spectra of CO adsorbed at low temperature on the Pd/ Al_2O_3 catalyst after different pretreatments are reported. Fig. 7 refers to the sample treated only by outgassing at 623 K. The spectrum is very different from that of the reduced sample recorded at r.t. (Fig. 6c). A strong sharp band is observed at 2151 cm^{-1} , not shifting significantly by outgassing. Outgassing at very low temperature causes the complete disappearance of the band, showing that it is due to a very labile species. The position of the band is

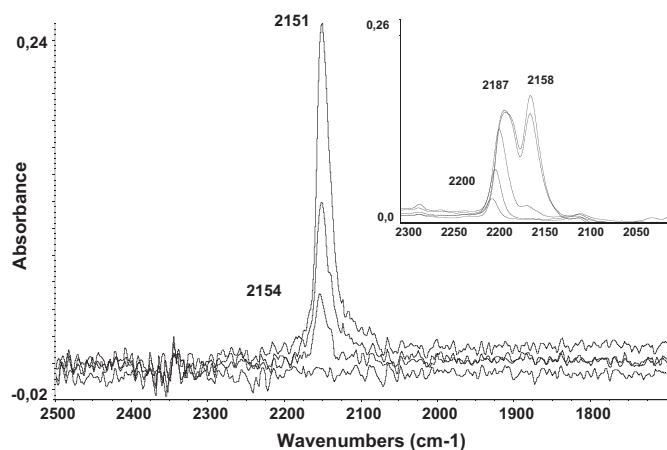


Fig. 7. FT-IR spectra of surface species arising from CO adsorbed at 133 K on 2% Pd/ θ - Al_2O_3 catalyst, after outgassing at 623 K. Outgassing upon warming from 133 K to 193 K. Inset: FT-IR spectra of CO adsorbed on θ - Al_2O_3 , in the same conditions. The activated surface spectra have been subtracted.

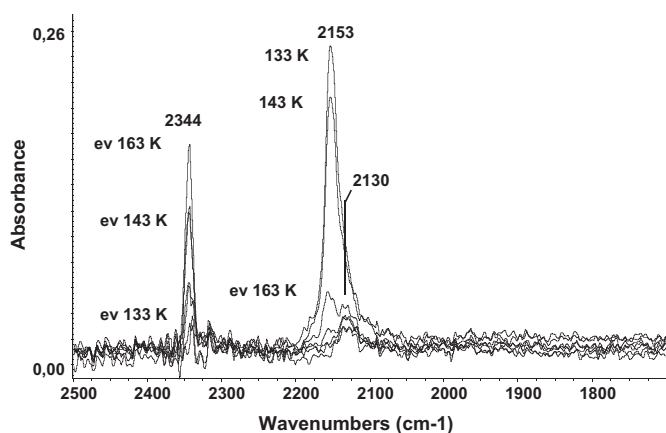


Fig. 8. FT-IR spectra of surface species arising from CO adsorbed on 2% Pd/ θ -Al₂O₃ catalyst, after reduction in hydrogen at 623 K. Outgassing upon warming from 133 K to –160 K. The activated surface spectra have been subtracted.

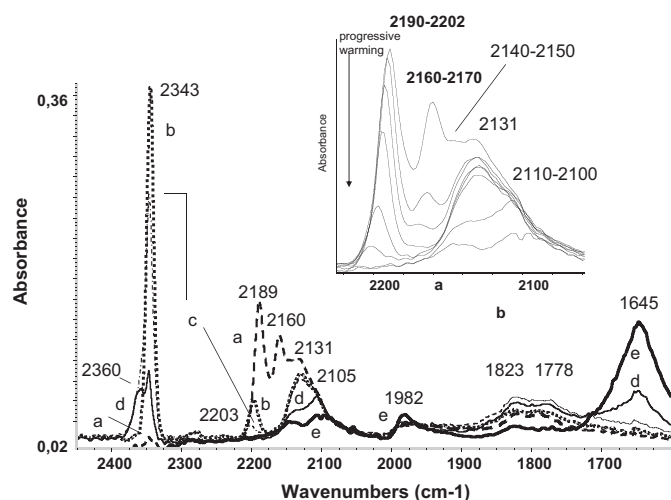


Fig. 9. FT-IR spectra of CO adsorbed on 2% Pd/ θ -Al₂O₃ catalyst, after reduction in H₂ at 773 K, contact with CO at 133 K and outgassing upon warming at (a) 133 K; (b) 193 K; (c) 233 K; (d) 273 K. The reduced surface spectrum has been subtracted. In the inset, continuously recorded spectra under outgassing upon warming, enlargement of the on-top carbonyl stretching region.

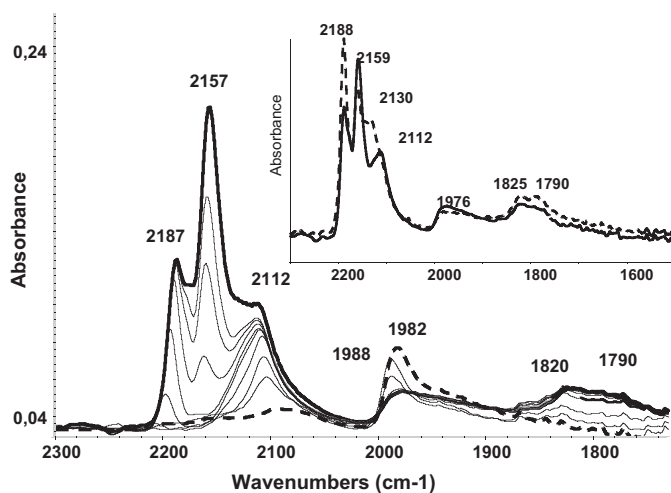


Fig. 10. FT-IR spectra of CO adsorbed on 2%Pd/ θ -Al₂O₃ catalyst, after prolonged treatment in H₂ at 773 K, contact with CO at 133 K (bold line) and outgassing upon warming to 273 K (broken line). The reduced surface spectrum has been subtracted. Inset: comparison between CO adsorbed at 133 K over mildly reduced (broken line) and reduced catalyst (bold line).

sufficiently shifted up from the typical position of CO stretching of liquid CO (2138 cm^{−1}) to show that carbon monoxide interacts with an electron-withdrawing centre. IR spectra of CO adsorbed at low temperature over pure alumina in these conditions (see the inset in Fig. 7) gives rise to two strong bands at 2158 and 2187 cm^{−1}. While the latter band disappears quickly by outgassing at <200 K, with a slight shift to 2165 cm^{−1}, the former resists outgassing up to near 0 °C, its maximum shifting up to 2200 cm^{−1} at very low coverage. The band at 2165–2158 cm^{−1} is typically assigned to CO hydrogen bonded to surface hydroxyl groups while the band at 2200–2186 cm^{−1} is assigned to CO interacting with Al³⁺ Lewis acid sites.

The spectrum of outgassed Pd/Al₂O₃ evidently does not show CO species interacting with Al³⁺ Lewis acid sites. Also, no bands at $\nu < 2130$ cm^{−1}, assignable to CO interacting with Pd metal centres, can be detected. The band at 2151–2154 cm^{−1} is also slightly but distinctly lower, in position, with respect to that of CO interacting with the OH groups of alumina, and the corresponding species seems also to be a little more labile. On the other hand, the spectrum after this outgassing pretreatment does not show (in contrast to what happens with alumina) bands due to surface OH's nor any relevant feature in the region 3800–3400 cm^{−1}, both before and after CO adsorption.

Thus, the band at 2151–2154 cm^{−1} may be associated with CO interacting with electron-withdrawing Pdⁿ⁺ species. Previous studies performed with higher-loading Pd/Al₂O₃ [28], showed that CO interacting with PdO particles just produce a band near 2150 cm^{−1}. In fact, XRD pattern of our sample show on the fresh sample the peaks of PdO together with those of the θ -Al₂O₃ phase. We conclude that Pdⁿ⁺ species and/or PdO particles are likely located just on the part of the alumina surface where the most reactive Al³⁺ and –OH sites are present, which are very likely those located on edges, corners or defects of the alumina crystals. In these positions the most acidic as well as the most basic sites are likely located. Pd ions and oxide ions should adsorb there and cover the alumina Lewis sites, exchanging and perturbing also the hydroxyl groups.

The spectra relative to CO adsorption after reduction in hydrogen (400 Torr) at 623 K for 1 h are reported in Fig. 8. Again a main band is observed at low temperature, centred at 2153 cm^{−1}, but it has now a pronounced component at 2130 cm^{−1}. The behaviour during outgassing at 140–200 K, however, is quite different than before. In fact the shoulder at 2130 cm^{−1} is evidently more resistant to outgassing than the main band, thus being apparently associated with a stronger interacting species. On the other hand, upon outgassing at 140–160 K a sharp band at 2344 cm^{−1} evidently grows. This sharp band is due to the OCO asymmetric stretching of adsorbed CO₂. This allows us to conclude that reduction in hydrogen at such a mild condition gives rise to new species whose interaction with CO gives rise to the absorption at 2130 cm^{−1}. This species should be that characterized by a strong oxidizing power, being able to produce CO oxidation in the absence of gas phase oxygen at ca 150 K. The position of the band at 2130 cm^{−1} is indicative of CO interacting with ionic Pdⁿ⁺ species. We can propose that slight reduction of PdO particles gives rise to PdO_x ($x < 1$) species which are able to interact more strongly with CO and to oxidize it at very low temperature.

After reduction treatment in hydrogen at 773 K, the spectra of CO adsorbed at –140 °C (Fig. 9) are definitely more complex. In the region of terminal CO stretching modes (2250–2000 cm^{−1}, see the inset in Fig. 9) we can distinguish 5 different bands. The highest frequency band, shifting from ca 2190 to above 2200 cm^{−1}, is certainly that of CO adsorbed on the alumina Lewis sites, reappearing after reduction and evident at low temperature. The lowest frequency one in this region is found in the region 2110–2100 cm^{−1} and is confidently assigned to terminal CO on Pd metal centres. However, additional bands are observed at 2160–2170, 2150–2140

and near 2130 cm^{-1} . These species are due to CO interacting with partially oxidized Pd centres, in agreement with previous literature reports [22]. Interestingly, by warming under outgassing, when these bands decrease in intensity with a rate which roughly inversely depends from the CO stretching wavenumber, a strong band at 2345 cm^{-1} , due to adsorbed CO_2 , first increases in intensity, then decreases when another new band at 1645 cm^{-1} starts to grow (Fig. 9). This behaviour suggests that strongly oxidizing Pd species exist and convert (at so low a temperature) CO into CO_2 , which further converts into carbonate species possibly by spill over the support. In fact the band at 1645 cm^{-1} is associated with weaker ones at 1445 and 1230 cm^{-1} , being all due to bicarbonate species.

The species responsible for the band in the region $2140\text{--}2150\text{ cm}^{-1}$ does not seem to be strongly oxidizing, being not associated with the formation of CO_2 . It can be due to CO adsorbed on nearly stoichiometric PdO, as discussed above. The band at $2160\text{--}2170\text{ cm}^{-1}$ has also been found over more heavily loaded Pd/ Al_2O_3 sample [28]. It could be associated with CO adsorbed on highly dispersed and highly ionic Pd^{n+} species, while that near 2130 cm^{-1} should be assigned, as above, to CO adsorbed on substoichiometric PdO_x species. It seems that this species is the most active in CO oxidation to CO_2 , that occurs just in parallel to the disappearance of this absorption.

During the experiment reported in Fig. 9 bands at 1982 , 1825 and 1790 cm^{-1} are also observed, typically due to bridging and threefold bridging CO on Pd metal particles. The band at 1982 cm^{-1} , certainly due to CO bridging over metallic Pd, grows by warming, while the features at 1823 and 1778 cm^{-1} , typically associated with multiply bridged CO in hollow sites, are observed at the lowest temperatures but decrease in intensity down to disappear by warming.

It is evident that a mild treatment in hydrogen at 773 K causes reduction of only part of PdO and PdO_x to Pd metal particles, as well as the displacement of Pd species that make free alumina Al^{3+} Lewis sites, and also surface OH's which are reappeared in the IR spectra. Pd metal particles tend to restructure during adsorption and partial reduction by CO. The possibility of high mobility of Pd carbonyl-like species causing sintering of Pd particles was already mentioned for catalysts supported on silica [29].

After more prolonged reduction in hydrogen at 773 K (Fig. 10) the spectrum of adsorbed CO is quite similar, but no oxidation of CO to CO_2 is observed. Actually, after this pre-treatment the bands at 2150 and 2130 cm^{-1} are also practically absent (see the comparison in the inset in Fig. 10). This would confirm that the feature at 2130 cm^{-1} corresponds to sites which are very active in CO oxidation at very low temperature.

We can note here that the pretreatment used before recording the spectra in Fig. 10 is the same as that used before recording the spectrum in Fig. 6c. The only difference is the temperature at which CO adsorption is performed and spectra are registered. The spectra in Fig. 10 (at 130 K and after outgassing upon warming at 300 K) and of Fig. 6c (room temperature adsorption without outgassing) are compared in Fig. 11. It is evident that the experiment performed at room temperature does not allow the detection of the high-frequency bands, which correspond to labile interactions. The spectrum recorded at room (and higher temperatures) only shows the stronger interactions.

After the experiment reported in Fig. 10, the same catalyst disk has been put into contact with water vapour 10 Torr at 473 K for 30 min . After further outgassing at the same temperature, CO was adsorbed again at 133 K . The spectra observed are those reported in Fig. 12. The spectrum is completely modified being now again similar to those reported in Figs. 7 and 8. A strong band is observed at 2151 cm^{-1} , that decreases in intensity by outgassing upon warming. In the inset A in Fig. 12 the CO stretching band observed after

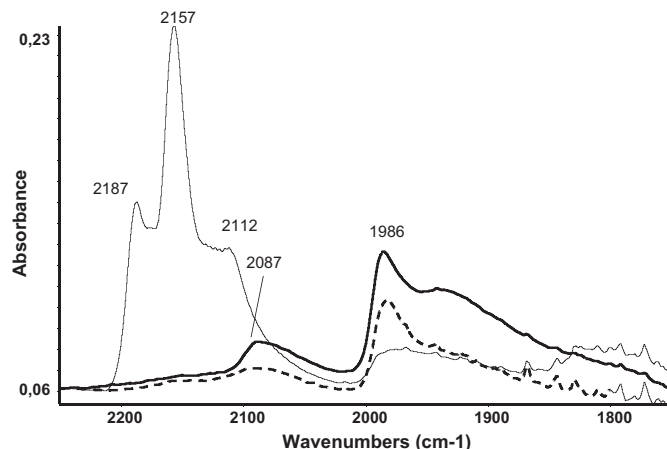


Fig. 11. FT-IR spectra of CO adsorbed on 2%Pd/ $\theta\text{-Al}_2\text{O}_3$ catalyst. Thin full line, after prolonged treatment in H_2 at 773 K and contact with CO at 133 K . Broken line, after following outgassing upon warming up to 300 K . Heavy full line: after prolonged treatment in H_2 at 773 K and contact with CO at 300 K (the same as Fig. 6c).

this experiment is compared with that observed after the experiment relative to Fig. 8. The shoulder at 2130 cm^{-1} is not so evident but the broader shape of the band implies that a component near 2130 cm^{-1} is present too. To the decrease in intensity of the main band, the growth of the band of adsorbed CO_2 at 2343 cm^{-1} corresponds. This experiment shows that water vapour can indeed act as an oxidant for Pd species, regenerating oxidized Pd^{n+} ions and active oxygen species which are those active in CO oxidation. On the other side, Pd metal particles are still present (see band at 1925 cm^{-1} , assigned to bridging carbonyl species, enlargement in Fig. 12B). We can note the position of this absorption is in the region where absorptions are found upon WGS reaction (Fig. 6).

The experiments described above provide evidence of how complex may be the surface of Pd/ Al_2O_3 catalysts after different reducing and oxidizing treatments, their interpretation based only on the presence of Pd metal particles and PdO particles (as usually done in most studies) being certainly an over-simplification. Partially reduced Pd oxide species may exist and are the most active in oxidizing CO to CO_2 at very low temperature ($140\text{--}240\text{ K}$). Under

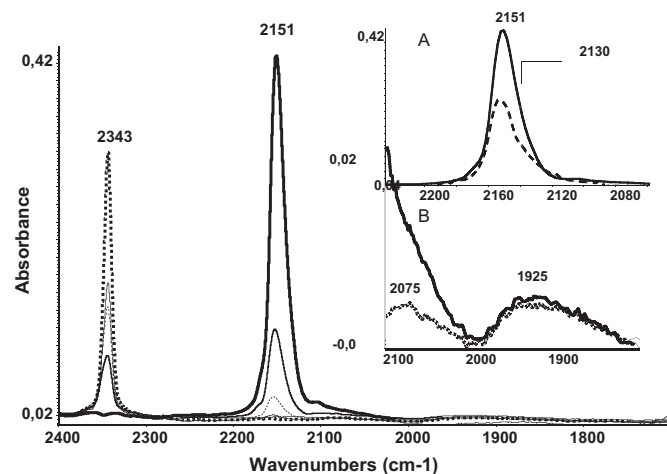


Fig. 12. FT-IR spectra of CO adsorbed on 2%Pd/ $\theta\text{-Al}_2\text{O}_3$ catalyst, after reduction in hydrogen at 773 K , re-oxidation in water vapor and following outgassing at 473 K . Contact with CO at 133 K (bold line) and outgassing upon warming to 193 K (broken line). The reduced surface spectrum has been subtracted. Inset A: magnification of the bridging carbonyl region. Inset B: comparison between CO adsorbed at 133 K over mildly reduced (broken line) and reduced catalyst (bold line).

these conditions IR spectra do not show the bands of formate nor carbonate species.

4. Discussion

The data described above allow some discussion on the active phases and the mechanisms of CO oxidation reactions over noble metal catalysts. Most literature concerning red-ox properties of supported metal catalysts refer on the presence of metal particles of different sizes and oxide particles and their interconversion. This is in part because those species are those can be quite easily detected with common techniques such as XRD and TEM. The idea that these species only are those involved in metal catalysis allows to discuss results in parallel with surface science studies of monocrystals, and use typical theoretical approaches for modeling. Our data show that this approach is an oversimplification. Actually the possible role of other surface species such as monoatomically dispersed metal or cationic centres or small clusters has been reported by many authors. In the review of Hadjiivanov and Vayssilov [22] it can be found that many authors interpreted IR data of CO adsorption on metal catalysts as evidence of the existence and action of dispersed metal species in supported catalysts. High resolution microscopy studies of Pt on alumina systems provide evidence of the existence of atomically dispersed Pt metal and of Pt₃ clusters [30]. According to Xiao and Schneider [31], atomically dispersed Pd and Pt on supports (α -Al₂O₃ in their case) can be quite easily oxidized and oxidation is also favored by support hydroxylation. Isolated zerovalent Pd centres can apparently be easily oxidized by oxygen to Pt²⁺, usually with the intermediacy of species like Cu⁺/Cu²⁺, as it occurs in the reoxidation step of the Wacker ethylene oxidation process also when carried out over solid catalysts [32].

Theoretical studies reported on the stabilization of highly uncoordinated Pt and Pd metal centres by alumina, providing a relevant difference of alumina-supported catalysts with respect to bulk metal surfaces [33]. Other studies report the existence of Pd particles decorated with a thin layer of an aluminate phase on Pd/Al₂O₃ supported catalysts [11]. The situation we found here for Pd/Al₂O₃ is similar to that previously found by Specchia et al. [34] for Pd/CeO₂-ZrO₂ and, also that recently described by Vedyagin et al. [35] for Pd/Al₂O₃ catalysts.

Several recent studies showed the presence of oxidized noble metal species, mostly together with reduced ones, over supported catalysts, apparently also in working conditions. This was the case, e.g. of Au/CeO₂ catalysts, where oxidized species appeared to be less active than metal particles in CO oxidation [36] and for supported Rh nanoparticles, that are more active than larger reduced particles [37]. As discussed by Ligthart et al. [37] the reaction order in CO for CO oxidation over noble metal catalysts is usually –1, as an effect of the strong adsorption of CO on large metal nanoparticles. However, it becomes close to zero for highly active Rh catalysts where smaller nanoparticles exist and are partly oxidized. This agrees with the weaker adsorption of CO on oxidized species, as found also in our case.

Reaction order for CO oxidation is somehow variable with CO concentration and reaction temperature over Pt [38,39] and Pd catalysts [38]. On Pt/Al₂O₃ catalysts it was found that partially oxidized catalyst shows enhanced activity in CO oxidation [40]. The oxidation and reduction of noble metal particles is certainly involved in the production of self-sustained oscillations during reaction, which can occur both on Pt/Al₂O₃ [41] and on Pd/Al₂O₃ [42]. In both cases, the maximum activity regime is attributed to a fully developed oxide state of the catalyst, and the lower activity regime to a CO covered metal state. These studies, however, do not take into account the high heterogeneity of the surfaces and their possible dynamic

behaviour, with the possibility of dispersion of oxide species and the existence of partially oxidized species.

Our results for supported noble metal catalysts [24–26], including those discussed here, show that the impregnation of alumina with Pd and Pt ions gives rise to a situation similar to that found also with several other metal ions impregnated over ionic supports (alumina, titania, zirconia). Metal cations, such as, e.g. alkali ions (e.g. K⁺ on alumina [43], transition metal ions (such as Mnⁿ⁺ on alumina [44] or Cuⁿ⁺ on alumina [45]) including vanadyl, molybdenyl and wolframyl cations [46], tend to spread (together with their counter anions) over the supports surfaces, diffusing over the more reactive support surface sites. These are defect sites such as corners and edges where highly coordinatively unsaturated cations (i.e. the supports Lewis acid sites) and anions (such as basic oxide and hydroxide species) are also located. At the lowest coverages the impregnated cations form atomically dispersed species strongly interacting with the support and, for this reason, stabilized in their cationic form. Only heavy reduction treatments allow their full reduction. These species in some way tend to neutralize the support surface, causing the disappearance of OH's and Al³⁺ cations.

Indeed, these dispersed species cannot usually be detected by many techniques, such as, e.g. normal TEM and XRD measurements, and even room or higher temperature CO adsorption experiments. Also theory cannot consider these species because actually most calculation techniques fail with defects and non periodic structures.

Only at higher coverages bulk or polyatomic oxide species form. These aggregated species are more easily reducible.

We report and discuss here two additional informations (i) at least some of the highly dispersed Pt and Pd cations are extremely active in oxidizing CO₂ at very low temperatures; (ii) these species disappear if a sufficiently strong reduction treatment is performed, but they can be reformed by reoxidation in moderate conditions not only by oxygen but also by water.

The overall picture is that highly dispersed Pt and Pd cations can be present (even when they are not detected with common techniques) in LT CO oxidation and LTWGS reaction conditions, and be the active sites, in Mars-Van Krevelen-type mechanisms.

5. Conclusions

IR studies performed at low temperature using CO as a probe reveal the existence of dispersed Ptⁿ⁺ and Pdⁿ⁺ cations and PdO_x species over Pd/Al₂O₃ and Pt/Al₂O₃ catalysts, likely “decorating” the defects of alumina crystals where they modify completely the behaviour of surface OH's and Lewis acid sites of alumina. Some of these species are the most active species as oxidant for CO already at ~200 K. These species are regenerated upon re-oxidation of deeply reduced catalysts both with oxygen and also with steam at moderate temperatures (~500 K). These species, although undetectable with most techniques in LT CO oxidation and WGS reaction conditions, could be active sites of these reactions in Mars-Van Krevelen type reaction paths. It seems likely that catalysts where highly dispersed noble metal species can be stabilized, can give rise to high activity in these reactions.

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